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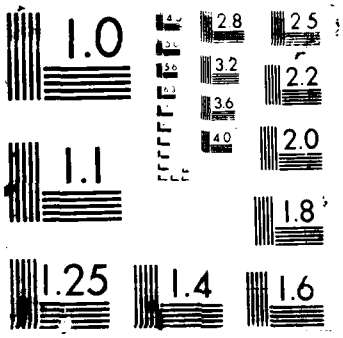
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Raman scattering, Brillouin scattering and optical harmonic generation are being used to probe the electronic properties of DNA. The conformation transitions, and physical properties such as stiffness, optical polarizability, and vibrational frequencies of the molecule in the solid state are found to be strongly dependent on the counter ion. We have examined the alkali metal salts of DNA, finding (for the monovalent counter ions) that the controlling parameter is the ion size. Properties are affected by the formation of bonds (possibly mediated by diffuse ion cloud interactions) between phosphate groups. We also find that the dynamics of the double helix are strongly influenced by the primary hydration shell at GHz frequencies. We have used Brillouin scattering to examine the dynamics of bound water, and Raman scattering to examine its structure. DNA films have unusual elasto-optic properties

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Annual report on "Optical Nonlinearity in DNA"

N000140-87-K-0478

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1. Introduction

This report summarizes a number of studies of DNA using optical probes. In the first part we give abstracts of work published (or in press) during year one. Notes are appended (where appropriate) to clarify the relationship to other work in the program. In the second part of the report, we outline some work in progress.

The research has two main goals. One is to probe the unusual electronic properties of DNA implied by our discovery of counter ion effects on the optical polarizability of DNA (Weidlich, Lindsay and Rupprecht, Biopolymers 26, 439 1987); this work has implications both for understanding the interactions of DNA, and for materials science applications. The experiments consist of direct measurement of optical nonlinearity by optical harmonic generation, and studies of the effects of counter ions on other properties which may be influenced by the electronic changes induced by counter ions. The second area of interest is the role that might be played by non-equilibrium phonons in the function of DNA (strand separation, for example). This second area has proved difficult. An extremely sensitive arrangement for low frequency stimulated Raman spectroscopy was set up and tried this year. Despite considerable improvement in Raman methods for pumping phonons (CARS), we have found the optical quality of the DNA too poor, and the signals too weak, for the proposed studies. On the other hand, there are several indications that the lowest frequency modes seen in the Raman spectrum are very anharmonic, and this has implications both for DNA dynamics and for the interpretation of low frequency spectra in general. We are probing these effects by making a survey of low frequency Raman spectra as a function of temperature.

We give abstracts of our work on low frequency Raman bands in section 2, followed by abstracts of our studies of the structure and dynamics of the DNA hydration shell in section 3. We then outline our (unpublished) initial studies of elasto-optic effects in DNA films (section 4). Work on optical harmonic generation is currently in progress, and will be described in the next report.

2. Counter-ion control of the properties of DNA: Low frequency Raman spectra.

2a: "The Origin of the A to B Transition in DNA Fibers and Films"

S.M. Lindsay, S.A. Lee, J.W. Powell, T. Weidlich, C. DeMarco, G.D. Lewen, N.J. Tao and A. Rupprecht, Biopolymers 27, 1015-1043 (1988).

Abstract

We have studied the hydration of Na-DNA and Li-DNA fibers and films, measuring water contents, x-ray fiber diffraction patterns, low frequency Raman spectra (below 100 cm^{-1}), high frequency Raman spectra (600-1000 cm^{-1}) and swelling, as a function of relative humidity. Most samples gain weight equilibrium (though not conformational equilibrium) in one day. The volume occupied by a basepair as the DNA is hydrated (obtained from x-ray and swelling data) shows anomalies for the case of Na-DNA in the

region where the A form occurs. Our Raman and x-ray data reproduce the well known features of the established conformational transitions, but we find evidence in the Raman spectra and optical properties of a transition to what may be a disordered B-like conformation in Na-DNA below 40% relative humidity.We have studied the effects of crystallinity on the A to B transition.We find that the transition to the B form is impeded in highly crystalline samples. (In most samples the transition occurs in three days (after putting the sample in 92% relative humidity) but in highly crystalline samples, the transition may take months. By comparing the Raman spectra of ordered and disordered films, we show that the amount of crystallinity determines the amount of A-DNA that is formed when ethanol is used to dehydrate the films. We show that rapid dehydration (by laser heating) does not result in a B to A transition. A fiber that gives A-like x-ray patterns probably contains B-like material in disordered regions. The low frequency Raman spectrum is dominated by a band at about 25 cm^{-1} in both Li- and Na-DNA. Another band is seen near 35 cm^{-1} in Na-DNA at humidities where the sample is A form In contrast to earlier reports, we find that the Raman intensity does not depend on sample orientation relative to the scattering vector. The 35 cm^{-1} band is largely depolarized whereas the 25 cm^{-1} band appears in VV, VH and HV polarizations. These bands are both weaker in HH polarization. The 25 cm^{-1} band may be due to a shearing motion of the phosphates and their associated counter ions, while the 35 cm^{-1} band may be characteristic of A crystallites. We consider mass loading, relaxational coupling to the hydration shell, and softening of the interatomic potentials as possible explanations of the observed softening of the low frequency Raman bands on hydration. Relaxation data suggest that added water binds tightly (on these timescales) and a mass loading model accounts for the observed softening rather well.

We conclude that the A to B transition is not driven by softening of the 25 cm^{-1} band. Rather it is most probably a consequence of crystal packing forces, with the more regular A form favored in crystals when these forces are strong.

Note: This paper describes the counterion mediated interhelical bonds which we believe to be important in determining many of the properties of solid DNA. These bonds may also be the site of ion interactions with the phosphates that lead to some of the unusual optical properties of DNA.

2b: "A Brillouin Scattering Study of the Hydration of Li- and Na-DNA films"
S.A. Lee, S.M. Lindsay, J.W. Powell, T. Weidlich, N.J. Tao and G.D. Lewen, Biopolymers, 26, 1637- 1665 (1987).

Abstract

We have used Brillouin Scattering to study the velocities and attenuation of acoustic phonons in wet-spun films of Na-DNA and Li-DNA as a function of the degree of hydration at room temperature. Our data for the longitudinal acoustic (LA) phonon velocity vs water content display several interesting features, and reveal effects that we can model at the atomic level as interhelical bond softening and relaxation of the hydration shell. The model for interhelical softening makes use of other physical parameters for these films, which we have determined by gravimetric, x-ray, and optical microscopy studies. We extract intrinsic elastic constants for hydrated Na-DNA molecules of $c_{11} \sim 8.0 \times 10^{10}$ dynes/cm^2 and $c_{33} \sim 5.7 \times 10^{10}$dynes/$cm^2$, which corresponds to a Young's modulus, $E \sim 1.1 \times 10^{10}$ dynes/cm^2 (with Poisson's ratio, $\sigma = 0.44$). The negative velocity anisotropy of the LA phonons indicates that neighboring DNA molecules are held together by strong interhelical bonds in the solid state. The LA phonon attenuation data can be understood by the relaxational model in which the

acoustic phonon is coupled to a relaxation mode of the hydration shell. Na-DNA undergoes the A to B phase transition at a relative humidity (rh) of 92%, while Li-DNA (which remains B form in this humidity range) decrystallizes at an rh of 84%. The Brillouin results for Na- and Li-DNA are remarkably similar, indicating that the A-B phase transition does not play a role in determining the acoustic properties of these two types of DNA.

Note: This paper develops a simple model for the ion-mediated interhelical interactions.

2c: "Counterion Effects on the Structure and Dynamics of Solid DNA"
T. Weidlich, S.M. Lindsay and A. Rupprecht (submitted to Physical Review Letters, May, 1988)

Abstract

We have measured the counterion species and concentration dependence of the low frequency Raman spectrum, speed of sound and the A-B transition in solid DNA. We find both the frequency of the lowest Raman active mode, and the water content at the A-B phase transition, depend strongly on ion size and concentration. Elastic constants show only a small dependence. These results indicate that ion-mediated interhelical forces control several important properties of solid DNA.

Note: These results show that it is not ion mass, but ion size (as measured by the parameter that describes closet approach of counter and co ion) that controls many properties of DNA. Charge is also important, and we are now investigating the divalent alkali metals.

2d: "Low frequency Raman Spectra of DNA: A comparison between 2 *oligonucleotide crystals and highly crystalline films of calf thymus* DNA" T. Weidlich, S.M. Lindsay, S.A. Lee, N.J. Tao, G.D. Lewen, W.L. Peticolas, G.A. Thomas and A. Rupprecht. In press, J. Phys. Chem.

Abstract

We have performed Brillouin and low frequency Raman experiments on the oligonucleotide crystals d(CGCGAATTCGCG) and d(GGTATACC). The Raman spectra below about 40 cm^{-1} are different from fiber spectra due to changes in crystal packing in the octamer, and small changes in interhelical interactions in the dodecamer. The modes between 50 and 120 cm^{-1} seem to depend more on intrahelical interactions rather than crystal packing forces. These modes may prove to be useful as marker bands for both interchain and intrachain interactions in oligonucleotide crystals and fibers.

Note: The overall shape of the spectra is remarkably similar in films and crystals. Therefore, the broad bandwidths cannot be caused by sequence heterogeneity or other environmental inhomogenieties, but may reflect inherently very anharmonic modes. This has implications both for the dynamics of DNA, and for the interpretation of the spectroscopic data in the first place. We are therefore studying a number of samples over a wide temperature range in an attempt to determine the origin of the lineshapes.

3. The Dynamics of the Hydration Shell by Brillouin Scattering

3a: "Dynamic Coupling between DNA and its Primary Hydration shell studied by Brillouin Scattering" N.J. Tao, S.M. Lindsay and A. Rupprecht, Biopolymers, in press.

Abstract:

We have measured the dispersion of phonon line widths between frequencies of about 2 and 10 GHz in DNA films at relative humidities between 0% and 95% The results show that the relaxation mode of the primary hydration shell retains its basic characteristics even in samples with very high water content. A modified mode coupling model is used to include both the collective nature of the sound wave, and to describe the change in hydration explicitly. It enables us to describe the coupling between the phonons and the water relaxation mode at various water contents, and allows us to extract values for the primary shell relaxation time and coupling constants over the range of hydration studied. The primary shell relaxation time (~ 40 ps) and coupling parameters remain nearly constant over the entire range of hydration. We have reanalyzed our earlier Brillouin data (taken as a function of temperature) in terms of two relaxation processes (primary plus a secondary shell contribution of about 2 ps at room temperature). This new analysis indicates that both processes follow a simple Arrhenius behavior with activation energies of 5 kcal $mole^{-1}$ for the primary shell and 7 kcal $mole^{-1}$ for the secondary shell.

We observe a rather broad central mode which can be fitted by a Lorentzian, and which may arise from direct (as opposed to coupled-mode) scattering from the primary relaxation mode.

Note: This work is of relevance to the problem of whether or not DNA sustains undamped vibrational modes at microwave frequencies. Our work suggests that it will not do so in the low GHz region, at least in solution. However, it is also possible that undamped coupled modes (with the primary shell) exist at a few tens of GHz. See also: "Comment on Microwave Absorption by dissolved DNA" N.J. Tao, S.M. Lindsay and A. Rupprecht, Phys. Rev. Lett. 59, 518 (1987).

and

"The active role of the DNA hydration shell" S.M. Lindsay and N.J. Tao in Structure and expression vol. 3: DNA and its drug complexes (eds M.H. and R.H. Sarma) Adenine, NY, 1988 pp 217 - 228.

3b: "Structure of DNA hydration shells studied by Raman spectroscopy" N.J. Tao, S.M. Lindsay and A. Rupprecht, submitted to Biopolymers, 1988.

Abstract

We have used Raman scattering to study the water OH stretching modes at ~ 3450 and ~ 3220 cm^{-1} in DNA films as a function of relative humidity (r.h.). The intensity of the 3220 cm^{-1} band vanishes as the r.h. is decreased from 98% to around 80%, which indicates that the hydrogen bond network of the water is disrupted in the primary hydration shell (which therefore cannot have an ice-like structure). The number of water molecules in the primary hydration shell was determined from the intensity of the 3200 cm^{-1} band as about 30 water molecules per nucleotide pair. The 3400 cm^{-1} OH stretch band persists at 0% r.h. implying that 5 to 6 tightly bound water molecules per nucleotide pair remain. The frequency of the 3400 cm^{-1} OH stretch mode is lower by about 30 to 45 cm^{-1} in the primary hydration shell compared to free water. The water content as a function of r.h. obtained from these experiments agrees with gravimetric measurements. The disappearance of the 3200 cm^{-1} band and the shift of the 3400 cm^{-1} band provide a reliable way of measuring the hydration number of DNA.

3c: "**Coupling of acoustic phonons in LiCl aqueos solutions to a relaxation mode of the ionic hydration shell and observation of central peaks in inelastic light scattering**" N.J. Tao and S.M. Lindsay, submitted to J. Phys. Chem.

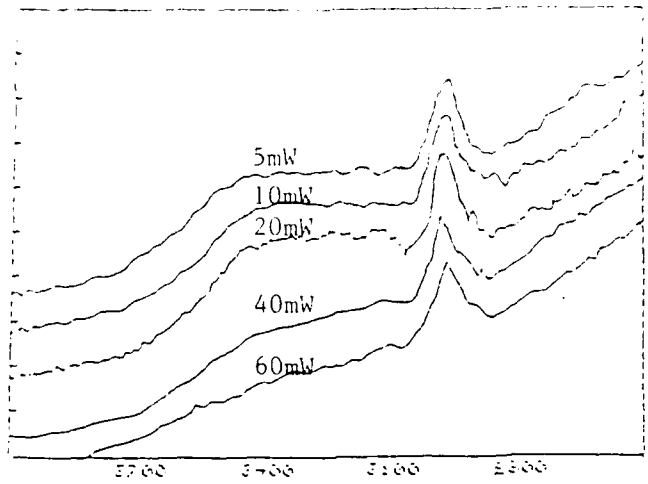
Abstract

We have measured Brillouin spectra of LiCl aqueous solutions as a function of concentration. A classical model of phonons damped by a viscous loss process does not describe the spectra adequately, They are better described by a coupled mode system, consisting of a phonon and a relaxation mode of water molecules in the ionic hydration shell. The hydration shell relaxation is well described by a single relaxation time which, for example, is 24 ps at 36 mole % LiCl. The relaxation time and the coupling strength depends on concentration, which indicates that the dynamic properties of the water molecules in the ionic hydration shells are affected by inter-ionic interactions.

Note: This simple system clarifies the interpretation of similar data from the more complex DNA system, although the water dynamics near simple ions turns out to be more varied!

4. Elasto-optic effects in DNA films

We have observed a strong dependence of the Brillouin shift (which is a measure of the speed of sound) on laser power, even at very low laser powers (see Hakim, Lindsay and Powell, Biopolymers 23 1185-1192, 1984). Our Raman spectra have not seemed to be so sensitive. The discrepancy cannot be due to some peculiar inhomogeniety in films, for it is even worse in the single crystals we have examined. Unfortunately, we are not able to examine Brillouin and Raman spectra simultaneously. However, with some care taken to set up optics carefully, the effect is perfectly reproducable for a given power density from sample to sample. It is complex, because it depends on illumination geometry and changes with counter ion (Na or Li). The spectra below were all taken with the same illumination optics. Fig. 1a shows Raman spectra from Na-DNA at 93 % r.h. as a function of laser power in the water OH stretch region. The sample does not start to dehydrate until laser powers of ~ 40 mW (note the 3400 cm^{-1} band). However, the Brillouin spectra show large changes. Some examples are given for Li and Na-DNA at 86% r.h. in the same (90°) scattering geometry (Fig. 1b) , and in backscattering (Fig. 1c). There is almost certainly no dehydration of the films up to 20 mW incident power in this geometry, yet the Brillouin shift for Na-DNA changes by about 25% (50% increase in elastic constants!), and by a similar amount for Li-DNA in 90° scattering, while Li-DNA in backscattering is not as strongly affected. We doubt that these effects are thermal (i.e., raising local temperature while, somehow, retaining hydration) as relatively large temperature increases - enough to dehydrate - are needed to affect the Brillouin shift by raising the sample temperature. These data suggest that an optically induced structural change of some sort is occurring. The effect is reminiscent of laser-induced freezing seen in liquid crystals (see Choudhury, Ackerson and Clark, Phys. Rev. Lett. 55, 833, 1985), but the optical geometry rules out a simple counterpart. Investigations continue.



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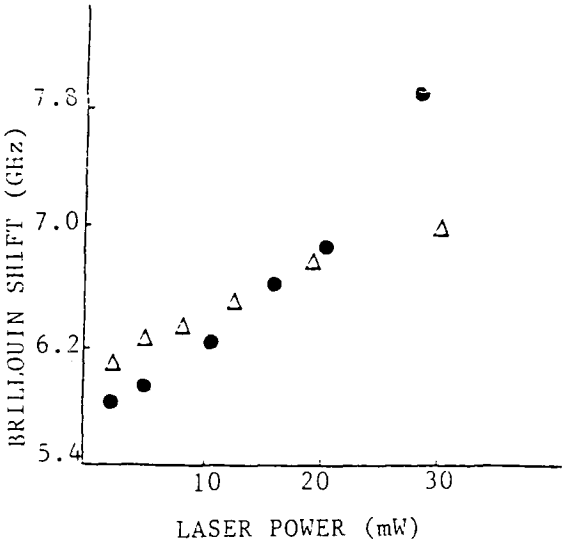

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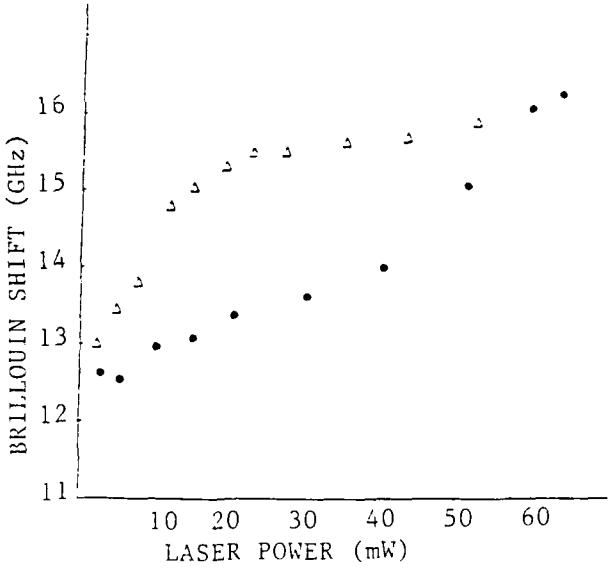

(C)

FIGURE 1

(A) Raman spectra vs laser power in the water OH stretch region. Dehydration occurs only after 20 mW. (B) and (C) Brillouin shift vs laser power (using the same optics) for 90° and 180° scattering respectively. Triangles are data for Na-DNA, circles are data for Li-DNA (both 86% r.h.).

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